PCT WORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau

INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification 6 : G11B 7/24 | A1

(11) International Publication Number: WO 97/08692

(43) International Publication Date: 6 March 1997 (06.03.97)

(21) International Application Number: PCT/EP96/03668

(22) International Filing Date: 21 August 1996 (21.08.96)

(30) Priority Data:
95202336.4 30 August 1995 (30.08.95) EP
(34) Countries for which the regional or international application was filed: NL et al.

(71) Applicant *(for all designated States except US)*: AKZO NOBEL N.V. [NL/NL]; Velperweg 76, NL-6824 BM Arnhem (NL).

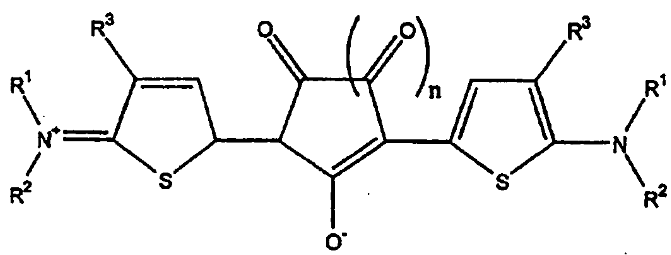
(72) Inventor; and
(75) Inventor/Applicant *(for US only)*: ERDHUISEN, Erwin, Wilhelmus, Petrus [NL/NL]; Van Goyenstraat 50, NL-6921 LG Duiven (NL).

(74) Agent: SCHALKWIJK, Pieter, Cornelis; Akzo Nobel N.V., Patent Dept. (Dept. APTA), P.O. Box 9300, NL-6800 SB Arnhem (NL).

(81) Designated States: CA, JP, KR, US, European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).

Published
With international search report.
Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.

(54) Title: OPTICAL RECORDING MEDIUM CONTAINING A THIOPHENE SQUARILIUM OR CROCONIUM DYE



(1)

(57) Abstract

The present invention is in the field of optical data media. More particularly, the present invention is directed to an optical medium comprising liquid-crystalline high-molecular weight material. The optical medium according to the invention comprises: a substrate, a recording layer, the recording layer comprising a high-molecular weight liquid-crystalline material which is at least partly homeotropically oriented and a dichroic dye according to formula (1), wherein R^1 represents an alkyl having 1-6 carbon atoms, phenyl, substituted phenyl, benzyl, oxyethyl, chloroethyl, cyanoethyl, or part of an alicyclic ring, such as a morpholine, piperidine or pyrrolidine ring; R^2 represents the same groups as R^1 and may be chosen independently from R^1; R^3 represents -H, phenyl, substituted phenyl, an alkyl having 1-6 carbon atoms, CN, CH, thienyl; n is 0 or 1. Surprisingly, it was found that these dyes have a very high dichroism and are readily, though not fully, oriented with the liquid-crystalline material. Further, they werefound te be readily soluble in various solvents and have lambda maxes in the wavelength area of 780-850 nm (the croconium dyes) or 610-700 nm (the squarilium dyes).

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AM	Armenia	GB	United Kingdom	MW	Malawi
AT	Austria	GE	Georgia	MX	Mexico
AU	Australia	GN	Guinea	NE	Niger
BB	Barbados	GR	Greece	NL	Netherlands
BE	Belgium	HU	Hungary	NO	Norway
BF	Burkina Faso	IE	Ireland	NZ	New Zealand
BG	Bulgaria	IT	Italy	PL	Poland
BJ	Benin	JP	Japan	PT	Portugal
BR	Brazil	KE	Kenya	RO	Romania
BY	Belarus	KG	Kyrgystan	RU	Russian Federation
CA	Canada	KP	Democratic People's Republic of Korea	SD	Sudan
CF	Central African Republic			SE	Sweden
CG	Congo	KR	Republic of Korea	SG	Singapore
CH	Switzerland	KZ	Kazakhstan	SI	Slovenia
CI	Côte d'Ivoire	LI	Liechtenstein	SK	Slovakia
CM	Cameroon	LK	Sri Lanka	SN	Senegal
CN	China	LR	Liberia	SZ	Swaziland
CS	Czechoslovakia	LT	Lithuania	TD	Chad
CZ	Czech Republic	LU	Luxembourg	TG	Togo
DE	Germany	LV	Latvia	TJ	Tajikistan
DK	Denmark	MC	Monaco	TT	Trinidad and Tobago
EE	Estonia	MD	Republic of Moldova	UA	Ukraine
ES	Spain	MG	Madagascar	UG	Uganda
FI	Finland	ML	Mali	US	United States of America
FR	France	MN	Mongolia	UZ	Uzbekistan
GA	Gabon	MR	Mauritania	VN	Viet Nam

OPTICAL RECORDING MEDIUM CONTAINING A THIOPHENE SQUARILIUM OR CROCONIUM DYE

The present invention is in the field of optical recording media. More particularly, the present invention is directed to an optical recording medium comprising liquid-crystalline high-molecular weight material.

Such an optical medium is described in EP-A1-0 608 924. In this document the liquid-crystalline material, a liquid-crystalline polymer, is homeotropically aligned, and a dichroic dye is co-aligned with the liquid-crystalline material. Because of this homeotropic orientation and the presence of the dichroic dye a high contrast is obtainable in relatively thin films, and is it possible to read out data via the difference in absorption. The read out and writing principles will be elucidated later.

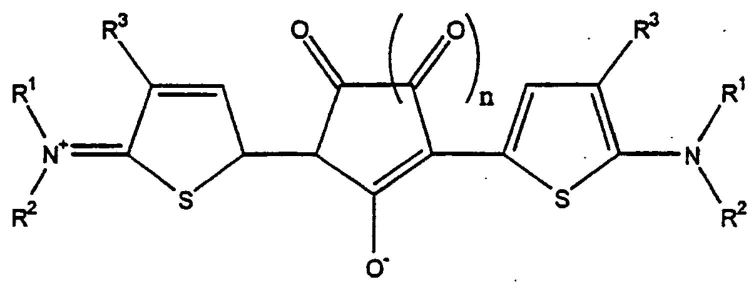
However, the dichroic dyes mentioned in the above-mentioned publication were found not to be optimally suited for this purpose for several reasons. For one thing, the dichroism of the dyes mentioned is not high enough. Other dyes known to have high dichroisms were found not to be absorbent in the wavelength area of 780-850 nm or 610-700 nm, as is necessary when solid-state lasers emitting in these wavelength ranges are used for reading the data. The first wavelength range is used for CDs which comply with the CD standard, the latter range is used for high density CDs.

Another problem is the poor solubility of the dyes in various solvents, causing segregation or crystallisation. All this resulted in optical media of poor contrast or with a blurred appearance due to dye segregation. The present invention provides an optical medium with improved contrast and without dye segregation.

To this end, the optical medium according to the invention comprises:

- a substrate,
- a recording layer,

the recording layer comprising a high-molecular weight liquid crystalline material which is at least partly homeotropically oriented and a dichroic dye according to the following formula:



(formula 1)

wherein:

- R^1 represents an alkyl having 1-6 carbon atoms, phenyl, substituted phenyl, benzyl, oxyethyl, chloroethyl, cyanoethyl, or part of an alicyclic ring, such as a morpholine, piperidine or pyrrolidine ring,
- R^2 represents the same groups as R^1 and may be chosen independently from R^1,
- R^3 represents -H, phenyl, substituted phenyl, an alkyl having 1-6 carbon atoms, CN, CH, thienyl
- n is 0 or 1

Surprisingly, it was found that these dyes have a very high dichroism and are readily, though not fully, oriented with the liquidcrystalline material. Further, they were found to be readily soluble in various solvents. The croconium dyes according to formula were found to have lambda maxes in the wavelength area of 780-850 nm, making them suitable for use in CDs according to the CD standard. The squarilium dyes were found to have lambda maxes in the wavelength area of 610-700 nm, makiing them suitable for use in high density Cds.

The croconium dyes according to formula 1 are known from DD-A5-294961. However, the properties rendering them suitable for use in the optical medium according to the invention, i.e., their extremely high dichroism, their solubility in various solvents, and their ability to co-orient with liquid-crystalline material, have not been acknowledged in this publication. The squarilium dyes are known from DD-A5-294962.

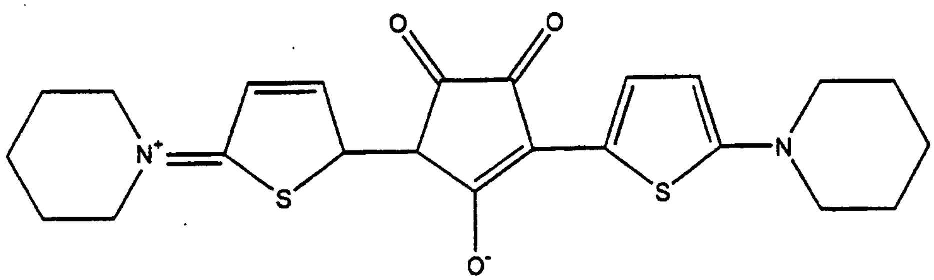
By optical media all types of optical media are meant, such as compact discs (CDs, both recordable and rewritable) or digital films. Digital films may have different shapes, e.g., tapes, cards, and discs which cannot be read as specified by the CD standard.

By high-molecular weight liquid-crystalline materials are meant liquid-crystalline polymers and liquid-crystalline glasses (molecular weight approximately 1000-2000). Suitable liquid-crystalline polymers are liquid-crystalline polyesters, liquid-crystalline polyurethanes, liquid-crystalline polyethers, liquid-crystalline polycarbonates, liquid-crystalline poly(meth)acrylates, liquid-crystalline polyimides, liquid-crystalline polyamides and liquid-crystalline polystyrene. Particular preference is given to liquid-crystalline side group polyethers and liquid-crystalline glasses because of their ready homeotropic orientation, suitable transition temperatures, good solubility, and good stability. For further information on liquidcrystalline polyethers reference may be had to Netherlands patent

application No. 9500503, which is incorporated herein by reference for all purposes. For further information on liquid-crystalline glasses reference may be had to Netherlands patent application No. 9500489, which is also incorporated herein by reference for all purposes.

Ordinarily speaking, a recordable film or CD is made by applying a solution of the liquid-crystalline material to the substrate and evaporating the solvent. Suitable substrates are PET, PET-ITO, metal, glass, cellulose acetate, polycarbonates, polycarbonate-aluminium, silicon, amorphous polyolefins (APOs), PMMA, etc. Generally, these substrates are provided with a thin layer of metal such as aluminium or gold. Preference is given to polycarbonate substrates, particularly for CDs, as it is relatively cheap and its properties are within the CD standard. APOs also have properties which lie within the CD standard, but these substrates are more expensive than polycarbonates. However, polycarbonate is liable to chemical attack by almost every solvent normally used for applying the liquid-crystalline material to the substrate, such as methyl ethyl ketone, cyclopentanone,

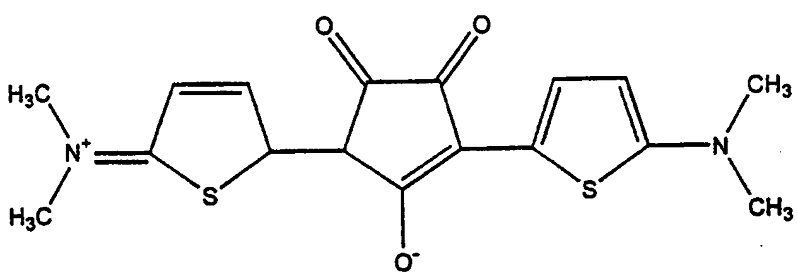
etc. Therefore, when use is made of polycarbonate substrates, it is necessary to employ a specific solvent for applying the liquidcrystalline material to the substrate: diacetone alcohol or tetrafuor-1-propanol. A specific advantage of the dyes according to formula 1 is their good solubility in diacetone alcohol and tetrafluor-1-propanol. Especially the dye according to the following formula was found to have a very good solubility in diacetone alcohol:



(formula 2)

Optical media having a dye according to formula 2 are preferred. When other substrates are employed, the conventional solvents can be used for applying the liquid-crystalline material to the substrate. The dyes according to formula 2 were found to be soluble in all these solvents.

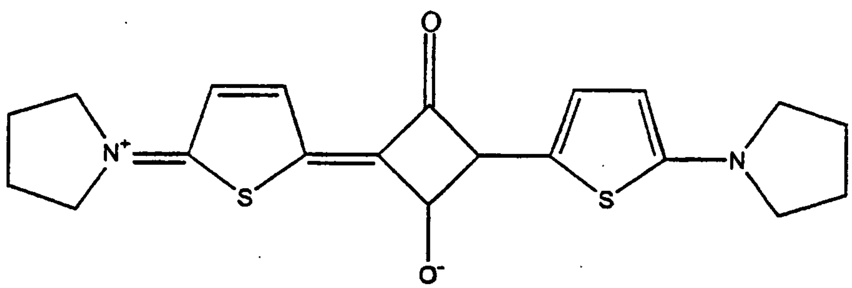
In another preferred embodiment of the invention a dye according to formula 3 is present:



(formula 3)

This dye was found to have a very suitable lambda max (763 nm) for use in CDs which are read with a laser having a -l of 780 nm, which is according to the CD standard. Further, this dye proved to be soluble in tetrafluor-1-propanol, which makes it suitable for use in CDs on polycarbonate substrates.

Dyes according to formula 4 as given below were found to have a lambda max of 662 nm and a dichroism of 6-7, making them pre-eminently suitable for use in high density CDs.



(formula 4)

The dichroic dyes according to formula 1 may be mixed or incorporated into the liquid-crystalline material. In the case of incorporation, the R-1 and R-2 groups must contain a functional group.

The reading out and writing principles will now be elucidated. When the film or CD contains dichroic dye, its orientation will be along the same lines as that of the mesogenic groups of the liquidcrystalline glass. The term dichroic dye refers to a dye which in an oriented medium (e.g., a nematic liquid-crystalline phase) will have a dichroic ratio (absorption ∥/absorption ⊥) > 1 in the desired wavelength range, absorption ∥ standing for the absorption of light which is polarised parallel with the orientation direction of the medium, and absorption -B standing for the

absorption of light which is polarised perpendicularly. Dichroic dyes, in other words, will absorb one polarisation direction of linearly polarised light to a much greater extent than the other one.
In a virgin homeotropically oriented film or CD the mesogenic groups, and hence the dichroic dye molecules, are oriented perpendicular to the film's surface, and there is only low absorption of the incident light by the dichroic dye molecules. (It should be noted that the polarisation direction of the light is perpendicular to its propagation direction as in many cases the incident light travels perpendicularly towards the film's surface). In the case of local heating or irradiation (e.g., with a laser) of the film or CD to above Tc, the homeotropic orientation is converted into an isotropic one. Rapid cooling causes this local isotropic orientation to be frozen in. In the case of such an isotropically written trace or pit, the dichroic dye molecules will likewise be isotropically oriented, resulting in a substantially higher absorption of the incident light. In the isotropic state 2/3 of the dichroic dye molecules -on average- is positioned with the long axis parallel with the CD surface (i.e, on average 1/3 along the x-axis of the plane of the film, and 1/3 along the y-axis). The polarisation direction of the incident light (either x- or y-polarised) is now parallel with the long axis of the dichroic dye molecules, and thus a high absorption is realised.

Writing out data with the aid of a laser requires that the liquidcrystalline material be, or be rendered, absorbing in the wavelength area of the writing laser. Generally, this is done by blending in or incorporating a suitable dye. Preferably, the same solid-state laser (λ 780-850 nm or 610-700 nm) is employed for writing as well as reading. In that case the dichroic dye according to the invention absorbs the laser light during writing and creates a difference in absorption during reading. Owing to the fact that the dyes according to formula 1 are highly dichroic but not fully oriented in the liquidcrystalline material, a sufficient amount of laser light can be absorbed during writing, and still a high contrast is obtained for reading.

Homeotropic orientation of the liquid-crystalline material can be attained in several ways:

1. By treating the surface of the substrate with homeotropic orientation inducing surfactants. These may be, int. al., silanes, higher alcohols, and the like, e.g., n-dodecanol and Liquicoat® PA, ex Merck.
2. By poling the liquid-crystalline layer in a magnetic or electric field. The electric field may be generated by corona poling (using a sharp needle or a thin wire as electrode). There will have to be a counter-electrode on the other side of the liquid-crystalline layer (e.g., an ITO-layer, a metal layer, or a conductive polymer layer), so that the poling field will be positioned over the liquid-crystalline layer. Alternatively, the liquid-crystalline layer can be provided with a conductive layer on either side, and an electric field applied thereto.

Both when homeotropic films are produced by means of a surface treatment and in the case of poling, the viscosity and the layer thickness of the liquid-crystalline film are of importance.

As described in EP application No. 94203398.6, the contrast of an optical medium may be improved by using the Fabry-Perot principle. In this case two reflecting layers have to be present of which the one on the substrate side should be partially transparent. The thickness of the liquid-crystalline material between the two reflective layers must be set carefully, so that the Fabry-Perot is tuned in the unwritten state and detuned in the written state, or vice versa. The present application is also directed to optical media according to the invention wherein the contrast has been improved by using the Fabry-Perot principle.

The invention is further illustrated by the following unlimitative examples.

EXAMPLES

The dichroism was determined by measuring the absorption of light polarised perpendicular to and parallel with the orientation direction of the film on a uniformly planar oriented film of the dye in a liquid-crystalline medium.

Example 1

The dyes according to formula 1 were prepared according to the method described in DD-A5-294 961, which is incorporated by reference for this purpose.

A dye was prepared according to formula 2 (dye 1), which was found to have the following properties: readily soluble in both diacetone alcohol and in tetrafluor-1-propanol; dichroism 8-9; a -λmax (DCM) of 798 nm; and ε of 230 000 l/mole.cm.

Example 2

Prepration of a liquid-crystalline glass (LC 1)
epoxide of cyanobiphenyl (epoxide 1)

A mixture of 39.0 g (0.20 mole) of hydroxycyanobiphenyl, 100 ml (1.25 moles) of epichlorohydrin, and 0.44 g (2.4 mmoles) of benzyl trimethyl ammonium chloride was heated to 70°C. Next, a solution of 17 g (0.42 mole) of sodium hydroxide in 100 ml water was dispensed in 3 hours. Following this addition there was one extra hour of stirring at 70°C. The reaction mixture was cooled to 20°C, and 200 ml of dichloromethane were added. The organic layer was separated from the aqueous one and washed with, successively, NaCl solution (twice) and water (twice). After drying on magnesium sulphate and concentration by evaporation

the crude product was converted to the crystallised form from 450 ml of methanol. The yield was 38.30 g (76%).

The epoxide of cyanobiphenyl was used to prepare a liquid-crystalline glass with 3,3'-sulphonyl dianiline, ex Aldrich® (SDA), by the following method:

A mixture of 1 eq. of SDA and 4 eq. of epoxy 1 was heated for 20 hours under a nitrogen atmosphere at a temperature of 130°C. The melt was cooled down and dissolved in THF, and the solution of approximately 20% (m/M) was precipitated in a 10-fold excess of ethanol. The yield was 95 %. The molecular weight was 1252, the Tg 106/111°C, the Tc 137°C, and the Tm 210°C.

Preparation of a CD-r

A solution of LC 1 and 1 wt% of dye 1 in diacetone alcohol was filtered and spincoated at 2000 rpm for 80 seconds on a grooved polycarbonate substrate having a thickness of 1.2 mm which was provided with a thin (appr. 8 nm) aluminium film. After drying at 40°C for 20 hours in a vacuum oven, the liquid-crystalline material was corona poled in an electric field. The liquid-crystalline layer was provided with a thick (100 nm) aluminium film by evaporation. The λ max of dye 1 in LC 1 was found to be 820 nm.

<u>Example 3</u>

Preparation of a liquid-crystalline polycarbonate (LC 2)

56.5 g (0.23 mole) 4-Cyano-4'-glycidoxy biphenyl and 5.7 g (0.025 mole) o-biphenyl glycidyl ether were dissolvied in 310 ml DMSO. 1.15 (10 mmole) potassium tert.butoxyde was added, and the solution was stirred for four days at room temperature.

The solution was precipitated in 2 l methanol and 5 ml water, after which the precipitate was filtered and dried in vacuo at 60°C. The yield was 61,8 g. The product was subsequently dissolved in 1,2 l CH_2Cl_2, and the solution was extracted with 300 ml water. The organic layer was dried over M_gSO_4 and evaporated. The yield was 53,8 g.

Preparation of a CD-r

A solution of LC 2 and 1 wt% of dye 1 in cyclopentanone was filtered and spincoated at 2000 rpm for 80 seconds on a grooved APO substrate having a thickness of 1.2 mm which was provided with a thin (appr. 8 nm) aluminium film. After drying at 40 °C for 20 hours in a vacuum oven, the liquid-crystalline material was corona poled in an electric field. The liquid-crystalline layer was provided with a thick (100 nm) aluminium film by evaporation. The λ max of dye 1 in LC 2 was found to be 820 nm.

Example 4

A dye according to formula 3 was prepared by the method described in DD-A5-294 961. Said dye was found to have the following properties: a λ max (TFP) of 763 nm, ????

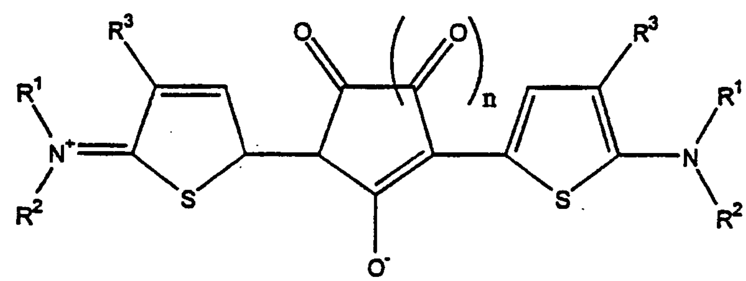
Example 5

A dye according to formula 4 was prepared by the method described in DD-294962. Said dye was found to have the following properties: a λ max (DCM) of 662 nm, ε of 370 000 l/mole.cm, D of 6-7.

CLAIMS

1. Optical medium comprising:
   - a substrate,
   - a recording layer,

   the recording layer comprising a high-molecular weight liquid crystalline material which is at least partly homeotropically oriented and dichroic dye according to the following formula:



(formula 1)

wherein:

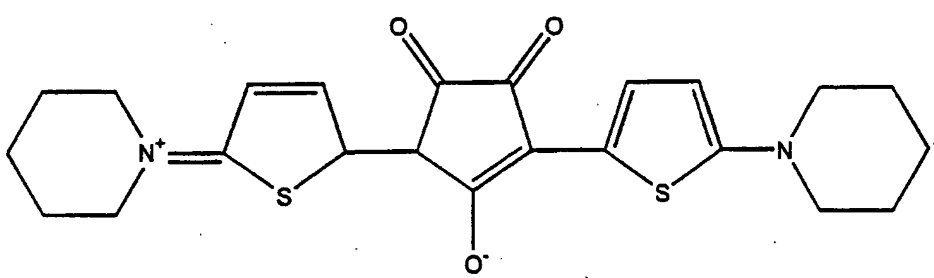
- R^1 represents an alkyl having 1-6 carbon atoms, phenyl, substituted phenyl, benzyl, oxyethyl, chloroethyl, cyanoethyl, or part of an alicyclic ring, such as a morpholine, piperidine or pyrrolidine ring,
- R^2 represents the same groups as R^1 and may be chosen independently from R^1,
- R^3 represents -H, phenyl, substituted phenyl, an alkyl having 1-6 carbon atoms, CN, CH, thienyl
- n is 0 or 1

2. Optical medium according to claim 1 wherein the liquid-crystalline material is a liquid-crystalline polymer.

3. Optical medium according to claim 1 wherein the liquid-crystalline material is a liquid-crystalline polymer glass.

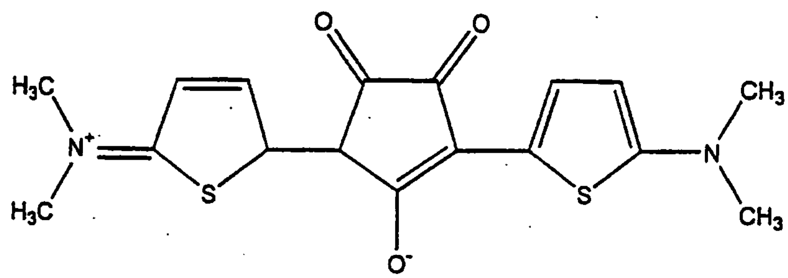
4. Optical medium according to claim 1 wherein the substrate is made of polycarbonate.

5. Optical recording medium according to claim 4 wherein the dichroic dye has the following formula:



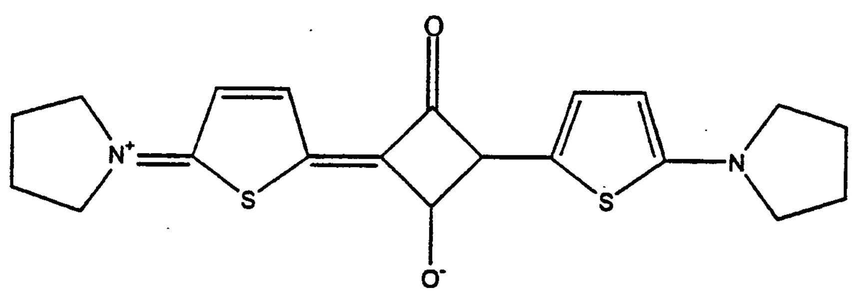
(formula 2)

6. Optical recording medium according to any one of claims 1-3 wherein the dichroic dye has the following formula:



(formula 3)

7. Optical recording medium according to claim 4 wherein the dichroic dye has the following formula:



(formula 4)

8. Optical recording medium according to any one of the preceeding claims wherein two reflecting layers are present on each side of the liquid-crystalline material, and the reflecting layer on the substrate side is partially

transparent, and wherein the thickness of the liquid-crystalline material between the two reflective layers is set so that the Fabry-Perot is tuned in the unwritten state and detuned in the written state, or vice versa.

INTERNATIONAL SEARCH REPORT

International Application No
PCT/EP 96/03668

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 G11B7/24

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 G11B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	EP 0 608 924 A (AKZO) 3 August 1994 cited in the application see the whole document ---	1-7
A	EP 0 478 052 A (AKZO) 1 April 1992 see page 5, line 19 - page 7 ---	1-7
A	DD 294 962 A (TECHNISCHE HOCHSCHULE "CARL SCHORLEMMER" LEUNA-MERSEBURG) 17 October 1991 cited in the application see the whole document ---	1-7
A	DD 294 961 A (TECHNISCHE HOCHSCHULE "CARL SCHORLEMMER" LEUNA-MERSEBURG) 17 October 1991 cited in the application see the whole document ---	1-7

-/--

[X] Further documents are listed in the continuation of box C.

[X] Patent family members are listed in annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

1

Date of the actual completion of the international search	Date of mailing of the international search report
12 December 1996	27.01.97

Name and mailing address of the ISA	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016	Heywood, C

INTERNATIONAL SEARCH REPORT

International Application No
PCT/EP 96/03668

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	DE 42 15 826 A (TECHNISCHE HOCHSCHULE "CARL SCHORLEMMER" LEUNA-MERSEBURG) 11 November 1993 see page 2, line 47 - line 53 ---	1-7
A	DYES AND PIGMENTS, vol. 17, 1991, BARKING GB, pages 19-27, XP002021063 H HORSTMANN ET AL: "SYNTHESIS AND CHARACTERIZATION OF 1,3-BIS-(2-DIALKYAMINO-5-THIENYL)-SUBSTITUTED SQUARAINES" see the whole document -----	1-7

1

Form PCT/ISA/210 (continuation of second sheet) (July 1992)

INTERNATIONAL SEARCH REPORT

Information on patent family members

Int ional Application No
PCT/EP 96/03668

Patent document cited in search report	Publication date	Patent family member(s)		Publication date
EP-A-608924	03-08-94	CA-A-	2114081	27-07-94
		CN-A-	1093731	19-10-94
		JP-A-	7041573	10-02-95
EP-A-478052	01-04-92	DE-D-	69106824	02-03-95
		DE-T-	69106824	31-08-95
		EP-A-	0615234	14-09-94
		ES-T-	2067848	01-04-95
		JP-A-	4283228	08-10-92
		US-A-	5525265	11-06-96
DD-A-294962		NONE		
DD-A-294961		NONE		
DE-A-4215826	11-11-93	NONE		